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14. ABSTRACT
During the reported period robust and sensitive techniques to produce and control ultracold polar KRb and RbCs as well as homonuclear Cs2 and Sr2 molecules have been developed. Factors that affect precision measurements and many-body quantum-collective experiments with these molecules have been analyzed. As part of these efforts the coherent transfer between weakly-bound Feshbach molecules and ro-vibrational ground state have been studied. In particular, high-precision calculations of the electronic potentials and transition dipole moments have been performed. Moreover, models for precision measurement of time variation of the proton-to-electron mass ratio using ultracold molecules in an optical lattice have been investigated by developing a zero-differential-Stark-shift optical lattice technique. The analyses included calculations of the molecular vibrational structure, lifetime of excited states, and Stark shifts of vibrational levels. Other accomplishments were the development of ab-initio methods for structural analysis of relativistic effects in heavy alkali-metal RbCs and Cs2 molecules. The research resulted in fifteen papers in refereed journals.

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ultracold molecules, optical lattice, electronic potentials, dipole moments, ro-vibrational structure, Stark shift, KRb, Sr2, RbCs, Cs2

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Final Performance Report

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In 2008 the Air Force Office of Scientific Research awarded grant FA9550-08–0106 to the principal investigator Professor Svetlana Kotochigova of Temple University. It is titled "*Precision Control of Ultracold Molecules in Optical Lattices*" and awarded for three years with one year no cost extention. During this time substantial progress towards the stated goals has been made.

The supported project was related to obtaining theoretical information on controlling the motion and state of ultracold homonuclear and polar molecules in optical lattices. The theoretical advances helped realize the experimental creation of vibrationally and translationally cold polar molecules and provided information on ultracold homonuclear molecules that can be used to conduct precision frequency measurements with the goal to find evidence for a possible time variation of the electron-proton mass ratio.

The proposal also included development of *ab initio* relativistic electronic-structure methods for structural analysis of small molecules. These methods were used for the theoretical study of polar alkali-metal KRb and RbCs molecules and homonuclear alkaline-earth Sr_2 and alkali-metal Cs_2 molecules. Understanding of observed spectra of these molecules was vital for these efforts. Detailed calculations were necessary to coordinate experimental efforts to form ultracold molecules in stable rovibrational levels of the ground state configuration. We worked out the most efficient way for production of vibrationally cold molecules either by Feshbach resonances or photoassociation of laser cooled K, Rb, Cs, or Sr atoms. Electronic structure calculations were combined with rovibrational calculations to obtain the observable characteristics of ultracold molecules. In addition, we evaluated the AC Stark shifts of rovibrational levels of the ground state potential and determined the optimal pathway for Raman transitions between these vibrational levels and electronically excited states.

The research resulted in fifteen papers in refereed journals. The fifteen papers are:

- K.-K Ni, S. Ospelkaus, M. H. G. de Miranda, A. Peér, B. Neyenhuis, J. J. Zirbel, S. Kotochigova, P. S. Julienne, D. S. Jin, and J. Ye, *A high phase-space-density gas of polar molecules in the rovibrational ground state*,
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- E. R. Hudson, N. B. Gilfoy, S. Kotochigova, J. M. Sage, and D. DeMille, *Inelastic collisions of ultracold heteronuclear molecules in an optical trap*,
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- D. DeMille, S. Sainis, J. Sage, T. Bergeman, S. Kotochigova, and E. Tiesinga, *Enhanced sensitivity to variation of m_e/m_p in molecular spectra*,
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- S. Ospelkaus, K.-K. Ni, M. H. G. de Miranda, B. Neyenhuis, D. Wang, S. Kotochigova, P. S. Julienne, D. S. Jin, and J. Ye, *Ultracold polar molecules near quantum degeneracy*,
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- O. Docenko, M. Tamanis, R. Ferber, T. Bergeman, S. Kotochigova, A. V. Stolyarov, Andreia de Faria Nogueira, and C. E. Fellows, *Spectroscopic data, spin-orbit functions, and revised analysis of strong perturbative interactions for the $A^1\Sigma^+$ and $b^3\Pi$ states of RbCs*,
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- Jianmei Bai, E. H. Ahmed, B. Beser, Y. Guan, S. Kotochigova, A. M. Lyyra, S. Ashman, C. M. Wolfe, and J. Huenneken, Feng Xie, Dan Li, Li Li, M. Tamanis, R. Ferber, A. Drozdova, E. Pazyuk, A. V. Stolyarov, J. G. Danzl, H.-C. Nagerl, H. Salami, and T. Bergeman, *Global analysis of data on the spin-orbit-coupled $A^1\Sigma^+$ and $b^3\Pi$ states of Cs_2*
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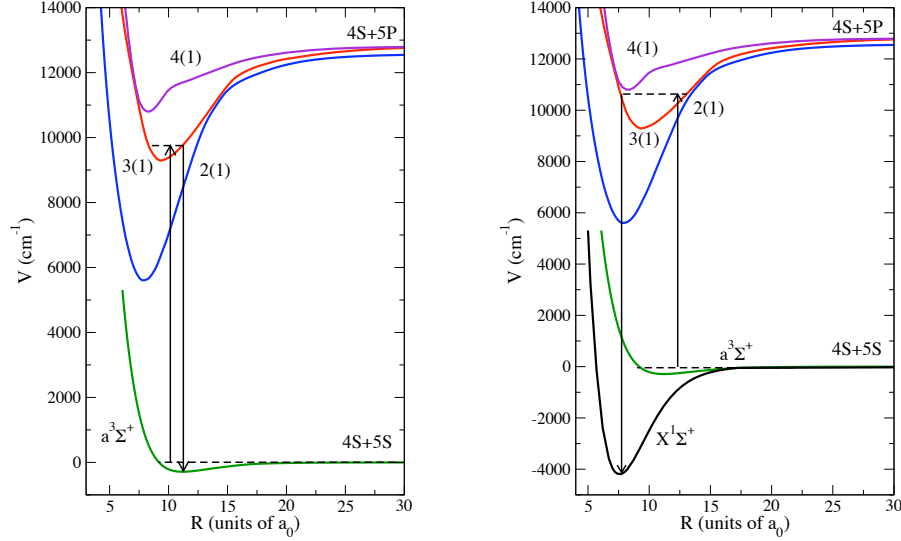 arXiv:1104.5478 (2011).

FIG. 1: Schematic of the KRb potential surfaces that are of interest in the experiment. The two panels show pathways to create ultracold polar molecules in the ground $a^3\Sigma^+$ state (left panel) and in the ground $X^1\Sigma^+$ state (right panel).

The studies were in support of experiments by groups of Dr. Jin and Dr. Ye at NIST/JILA, by the group of Dr. DeMille at Yale University, and by group of Dr. Hudson at UCLA. A more detailed description of results is given below.

A. Theoretical modeling of an efficient state transfer into an ultracold dense gas of KRb molecules

Our theoretical work on the coherent Raman transfer between weakly-bound Feshbach KRb molecules and the rovibrational ground state of this molecule has contributed to the successful creation of a high phase-space-density gas of polar ^{40}K ^{87}Rb molecules at JILA. These successful developments are summarized in joint papers in Nature Physics and Science. In these works we searched for an efficient production mechanism using a multi-channel description of the initial, intermediate, and final states of the transfer. A schematic of this transfer is shown in Fig. 1.

Our calculations find a non-degenerate hyperfine and Zeeman structure of the singlet $X^1\Sigma^+$ and triplet $a^3\Sigma^+$ ground states in a magnetic field B. The findings are consistent with the observations at JILA. The theoretically predicted levels are shown in Fig. 2 by horizontal lines, while the experimentally observed rotational, hyperfine and Zeeman levels are marked by crosses and triangles. The horizontal axis orders the levels by the conserved projection angular momentum M_F. The comparison of theory and experiment indicates that our coupled-channel calculation is very accurate.

We also focused on the need to use a multi-channel description the vibrational structure of the excited electronic potentials. The origin of the coupling is the relativistic spin-orbit interaction, which mixes states with different total molecular electron spin. Ie. states with singlet or triplet character. In turn this coupling allows dipole transitions that are otherwise
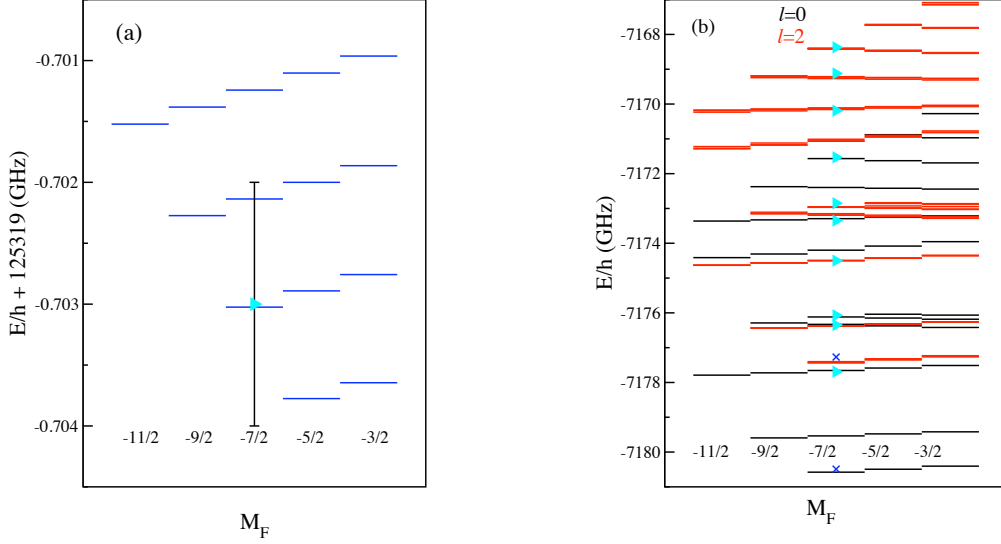
FIG. 2: Panel (a) shows the hyperfine and Zeeman structure at $B=545.9$ G of the $v=0$ $\ell=0$ level of the singlet $X^1\Sigma^+$ state of $^{40}K^{87}Rb$; Panel (b) shows the $\ell=0$ and 2 rotational levels of the $v=0$ vibrational state of the triplet $a^3\Sigma^+$ potential. The crosses and triangles indicate the experimentally observed energies. The levels are grouped by the projection quantum number M_F.

forbidden. Vibrational levels of intermediate triplet potential can couple to the final singlet ground state. The previously unknown spin-orbit coupling matrix elements and electronic dipole moments were obtained from our electronic structure calculations. Figure 3 shows examples of vibrationally-averaged transition dipole moments. The intermediate vibrational level used by experimentalists at JILA in the coherent transfer is indicated by $v = 23$.

B.   Prospects for application of cold Sr_2 molecules in precision measurements

In general, molecules exhibit a complex internal structure and dynamics due to vibrations and rotations of their constituent atoms. This nuclear motion depends on the potentials created by electron motion. For example, properties of highly-excited vibrational levels are mainly determined by atomic properties, whereas properties of deeply-bound vibrational levels are determined by the electronic bonding of molecule. They reveal fundamental forces of different origin within one system. Therefore, frequency-difference measurements between weakly and deeply-bound vibrational levels can be a sensitive tool for testing fundamental forces.

During the reported period we performed a detailed analysis of various factors influencing frequency measurements between vibrational levels of the ground state of the Sr_2 molecule in the presence of an optical lattice. The analysis includes calculations of two-photon transition dipole moments between deeply and weakly bound vibrational levels, lifetimes of intermediate excited states, and Stark shifts of the vibrational levels by the optical lattice field, including possibilities of Stark-cancellation trapping. The left panel of Fig. 4 shows two-photon vibrationally averaged dipole moments for the Raman transition as a function of
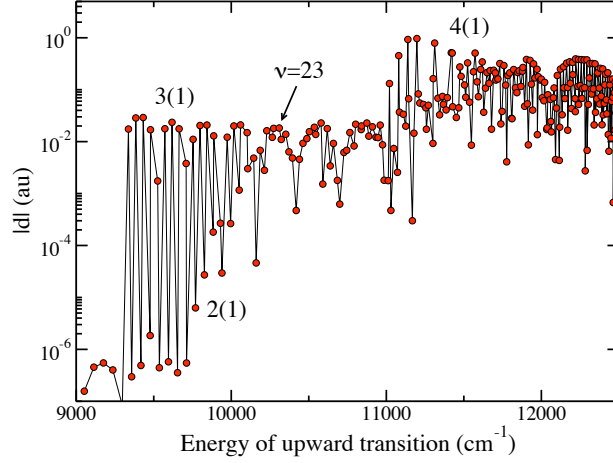
FIG. 3: Transition dipole moment from the $v=0$, $J=0$ X$^1\Sigma^+$ level to mixed vibrational states of three excited $\Omega=1$ potentials of the ^{40}K^{87}Rb molecule as a function of the upward transition energy to the excited states. The bound $v=23$ level of the predominantly $3(1)$ state is marked and used as intermediate state in Fig. 1.
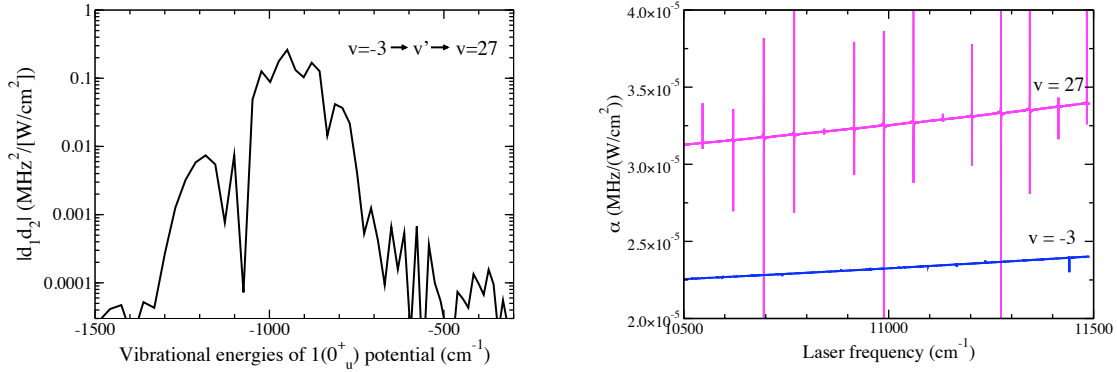

FIG. 4: Left panel: Two-photon vibrationally averaged dipole moment for the Raman transition between the $v = -3$ and $v = 27$ vibrational levels of the X$^1\Sigma_g^+$ state of Sr$_2$ as a function of vibrational energy of its $1(0_u^+)$ intermediate state. The $v = 27$ level is the 28th vibrational level counting from the bottom of the X potential. The $v = -3$ level is third most-weakly bound vibrational level. The X state has on the order of 60 vibrational levels. Right panel: Dynamic polarizability of the $v = -3$ and $v = 27$, $J=0$ vibrational levels of the X$^1\Sigma_g^+$ state of Sr$_2$ as a function of laser frequency near 11000 cm^{-1}. Stark cancellation occurs when the polarizability of the two vibrational levels is the same. Even though the resonances are narrow on the scale of the figure, their width is sufficiently large to be practical for experiments. The resonances in the polarizability of the $v = 27$ level are due to transitions to the $1(1_u)$ intermediate excited potential.
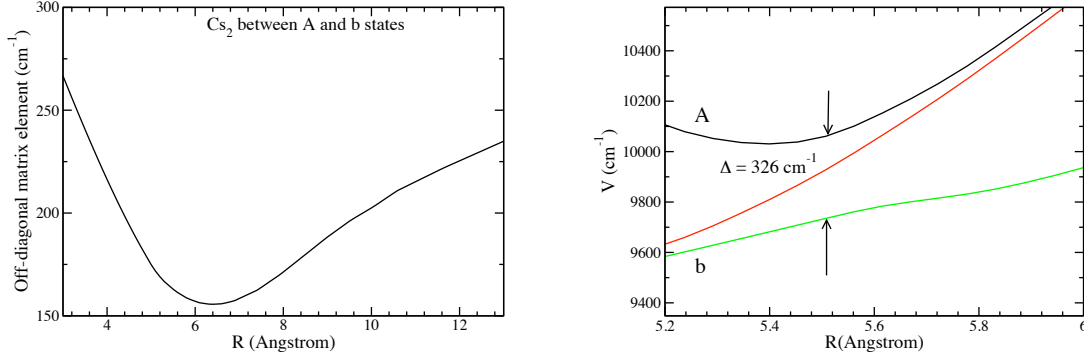
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FIG. 5: Left panel: *ab initio* off-diagonal spin-orbit function Δ_{od} between the $A^1\Sigma_u^+$ and $b^3\Pi_u$ states obtained by a non-relativistic calculation. Right panel: avoided crossing of two relativistic $\Omega^\pm = 0^+$ potentials of Cs_2 belonging to the $A^1\Sigma_u^+$ and $b^3\Pi_u$ non-relativistic configurations near $R=5.5$ Å. The closest approach between the two potentials equals 326 cm^{-1} and corresponds to twice the value of the off-diagonal spin-orbit function at 5.5 Å. The red curve is the $\Omega^p = 0^-$ component of the $b^3\Pi_u$ potential.

vibrational energy of the $1(0_u^+)$ intermediate state.

Trapping ultracold molecules in optical lattices using ac Stark shifts is key for optimized control and precision. For example, a Stark-cancellation, or *magic frequency*, technique has enabled state-of-the-art neutral atom clocks. This approach relies on a suitable crossing of dynamic polarizabilities of the two probed states at a particular lattice wavelength. This ensures a zero differential Stark shift and a suppression of inhomogeneous Stark broadening. This cancellation can be sought for specific pairs of vibrational levels. For example, tuning the lattice frequency near a narrow resonance of Sr_2 associated with an optical transition from a vibrational level of $X^1\Sigma_g^+$ to a level of the $1(1_u)$ potential can help achieve matching polarizabilities of a vibrational level pair of the $X^1\Sigma_g^+$ state. The right panel of Fig. 4 shows examples of these cancellations for two vibrational levels of the $X^1\Sigma_g^+$ state of Sr_2.

C. Study of the RbCs and Cs_2 molecules, critical for a physical realization of highly controlled molecular systems in optical lattices

As part of efforts towards precision measurements and the coherent transfer between weakly-bound Feshbach molecules to the rovibrational ground state high-precision calculations of the electronic potentials and transition dipole moments for the RbCs and Cs_2 molecules were performed. In addition, the previously unknown spin-orbit coupling matrix elements of low excited states were calculated.

For the proposal a MR-RAS-CI method was developed and applied to calculate various molecular properties. It partitions occupied and unoccupied electronic orbitals into subsets, which are used to construct the molecular electronic wave function. Molecular Hartree-Fock (Dirac-Fock) wave functions are used to describe occupied core and valence orbitals. Since the radius of the Hartree-Fock orbitals grows rapidly with the level of excitation the

spatial overlap between orbital in the CI expansion becomes progressively leading to slow convergence. To improve convergence we use Sturm-functions to form excited unoccupied virtual orbitals.

Spin-orbit coupling between electronic potentials that converge to the same nonrelativistic dissociation limit plays an essential role for a proper description of the molecular dynamics. At short and intermediate internuclear separations, where the electrostatic and exchange interactions between atoms are nonzero, we use perturbation theory starting from the non-relativistic Born-Oppenheimer approximation to calculate spin-orbit matrix elements. At long-range it is more appropriate to rely on relativistic electronic structure.

We have performed both a non-relativistic as well as a relativistic electronic structure calculation in order to make comparisons. In particular, the strength of the spin-orbit coupling between the $A^1\Sigma_u^+$ and $b^3\Pi_u$ potential of RbCs and Cs_2 has been characterized. For the non-relativistic CI calculation we have evaluated of matrix elements of the spin-orbit operator

$$\hat{H}_{SO} = \frac{\alpha^2}{2} \sum_N \sum_i \frac{Z_N}{r_{iN}^3} \vec{l}_i \cdot \vec{s}_i - \frac{\alpha^2}{2} \sum_{i \neq j} \frac{1}{r_{ij}^3} [\vec{r}_{ij} \times \vec{p}_i] \cdot (\vec{s}_i + 2\vec{s}_j), \tag{1}$$

where α is the fine structure constant and $\vec{s}_i$ is the spin of electron i. The first term of Eq. (1) is an one-electron operator that describes spin-orbit couplings between one nuclei and one electron. Here r_{iN} is the separation between the i-th electron and nucleus N with charge Z_N and $\vec{l}_i$ is the electron orbital angular momentum relative to nucleus N. The second term of Eq. (1) is a two-electron operator describing the spin-orbit coupling between electrons. Here $\vec{r}_{ij}$ is the separation between electrons i and j and $\vec{p}_i$ is the momentum of electron i.

As an example, the off-diagonal spin-orbit matrix element from the non-relativistic calculation of Cs_2 is shown in Fig. 5(left panel). We found that the one-electron spin-orbit operator of Eq. (1) provides ~ 99 % of the total value of the spin-orbit coupling.

The result of the relativistic calculation is shown in Fig. 5(right panel). The relativistic spin-orbit interaction leads to an avoided crossing between the A and b potentials. The smallest energy difference ΔE occurs at $R = 5.5$ Å and is equal to 326 cm^{-1}, twice the value of the off-diagonal spin-orbit function Δ_{od} (left panel) at this internuclear separation. A comparison of Δ_{od} at R $= 5.5$ Å obtained by the non-relativistic and relativistic calculations shows good agreement.